



Observation of Individual Fluorine Atoms From Highly Oriented Poly(tetrafluoroethylene) Films by Atomic Force Microscopy

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TECHNICAL MEMORANDUM

OBSERVATION OF INDIVIDUAL FLUORINE ATOMS FROM HIGHLY ORIENTED POLY(TETRAFLUOROETHYLENE) FILMS BY ATOMIC FORCE MICROSCOPY

1. INTRODUCTION

In recent years, there has been an increasing interest in properties of unidirectional materials grown on highly oriented polymer surfaces such as the poly(tetrafluoroethylene) (PTFE) films coated onto smooth glass surfaces. The technique for depositing a highly oriented, thin film of PTFE as a substrate for oriented growth of materials was first demonstrated by Wittmann and Smith.¹ In this technique, a thin PTFE film is deposited by sliding or rubbing a Teflon[®] bar over a heated glass surface at a specific temperature. Depending on the pressure, temperature, and sliding rate, the thickness of deposited layers can be varied from 30–150 Å. The PTFE-coated substrate is simple yet surprising versatile for oriented growth of many organic, inorganic, and polymer compounds. The significant aspect of PTFE films is their unusual ability to molecularly align a wide variety of materials grown onto them from solution, melt, or vapor-phase deposition, at temperatures below the melting point of PTFE (≈ 340 °C). Electron diffraction studies of these films revealed that the PTFE macromolecules are oriented parallel to each other along the sliding direction.¹

Atomic force microscopy (AFM) has been used as a powerful scanning probe technique for surface analysis for a variety of materials with nanometer-scale resolution in air and even under liquids at ambient conditions.^{2–4} While scanning tunneling microscopy was developed first and is widely used for metal and semiconductor materials, AFM is a novel tool for the analysis on nonmetallic materials. AFM technique does not require special interactions between the probe tip and the analyzed material surface such as conducting current, tunneling current, magnetic forces, etc. Therefore, AFM investigations of thin films and crystals of polymers and polymer-related compounds have been conducted in the early 1990's.^{5–7} Recently, the AFM studies of PTFE film thickness and molecular structure performed by Hansma et al.⁸ and Magonov et al.⁹ were particularly noteworthy. However, image resolution from these studies was not sufficient to distinguish clearly the individual fluorine atoms from the PTFE macromolecular chains. Reported in this paper are the first direct observations of individual fluorine atoms, and the measurement of the fluorine-helix and carbon-helix radii from highly oriented PTFE films using AFM.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of PTFE Samples

Highly oriented PTFE thin films, prepared uniquely by frictional transfer method, have been described by Wittmann and Smith.¹ Briefly, the method consists of using smooth microscope glass slides as hot substrates, and PTFE film is deposited by sliding a solid PTFE bar (Teflon) against the substrate's surface at a specific temperature, contact pressure, and sliding speed. Typically, the temperature of the glass surface is about 130 °C, the sliding rate is 1 mm/sec and the pressure is 1 kg/cm². Depending on the pressure, temperature, and sliding rate the thickness of deposited layers can be varied from 30–150 Å. Using this technique, the chain axes of the PTFE macromolecules can be made to orient in the sliding direction. The PTFE-coated glass slides were obtained from UNIAX Corporation in Santa Barbara, CA.

2.2 AFM Techniques

The PTFE films were imaged using an AutoProbe® CP system from Park Scientific Instruments (PSI), Inc., which was fitted with a scanner, having a maximum scanning size of 100 µm. The AFM microscope was calibrated in *x* and *y* scanning directions by imaging the well-known hexagonal structure of muscovite mica, which has a lattice spacing of 5.20 Å. All AFM images were taken in air using two contact modes: topography (constant force mode) and error signal (constant height mode). The AFM scanning probe consists of a pyramidal silicon nitride microtip, which is mounted at the end of a V-shaped microcantilever with a low spring constant. The typical radius of curvature for a sharpened tip is <200 Å, and the microcantilever is ≈180 µm long and 0.60 µm thick, having a spring constant of 0.05 N/m and a resonant frequency of 22 kHz. Figure 1 is a schematic of the AFM setup.

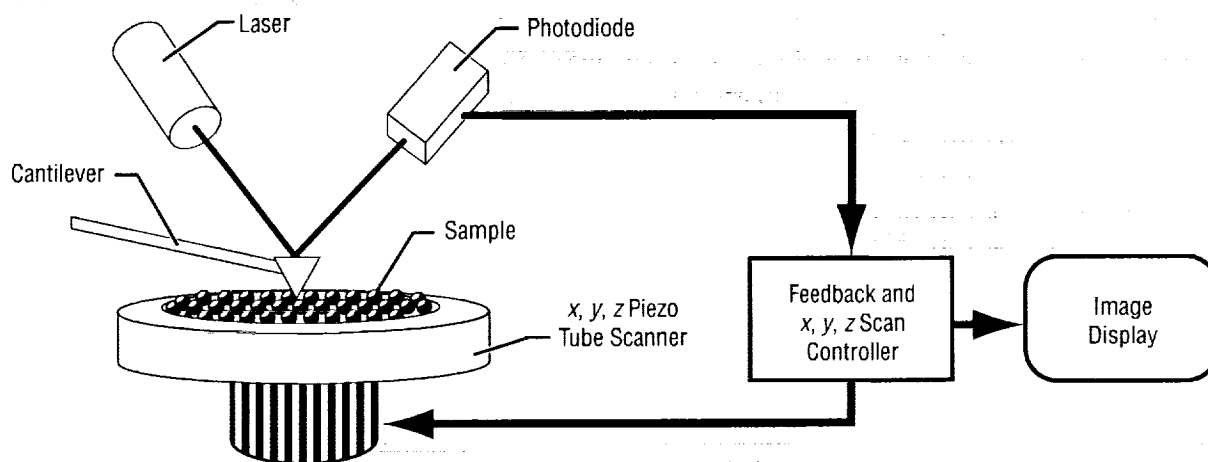


Figure 1. Schematic for a typical AFM experimental setup

3. RESULTS AND DISCUSSION

3.1 Film Thickness and Morphology

Figure 2 shows an AFM image, with a $5 \times 5 \mu\text{m}$ field of view, of a highly oriented PTFE film deposited onto a glass surface. The image is electronically processed using software in the flatten mode to remove undesirable curvatures and slopes which can appear in the image. These image distortions are produced mostly from the bending motions of the scanner as it rasters the sample relative to the microcantilever tip. The film thickness variation can be estimated using a gray-scale indicator bar, which is shown on the left side of the figure. Using this technique, the chain axes of the PTFE macromolecules can be made to orient in the sliding direction. The PTFE film appears to have a typical row-like structure, oriented in the vertical direction of the image, and the film covers the glass surface almost completely. However, about 5–10 percent of the glass surface is still visible between these PTFE rows. Interestingly, the uncovered parts of the glass substrate, which are shown as vertical black lines, are unique image features that can be utilized for film thickness measurements. As shown in figure 2, a cross-sectional line, taken perpendicular to the orientation of the film near the center of the figure, was chosen as a location where the glass slide surface is visible. In this case, the difference between the mean value of the film height distribution and the glass substrate would give the average thickness of the film.

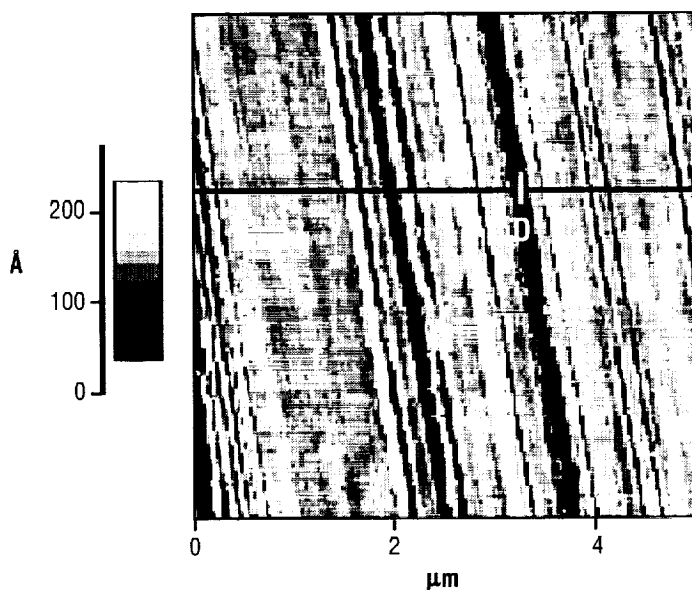


Figure 2. AFM image of a highly oriented PTFE film deposited on glass substrate with a $5 \times 5 \mu\text{m}$ field of view. The film appears to have a row-like structure, oriented in the vertical direction of the image.

Depending on the pressure, temperature, and sliding rate, the thickness of deposited layers can be varied from 30–150 Å. Figure 3 shows the film thickness distribution curve located at this cross-sectional line, and the average thickness was ≈ 120 Å. In addition, figure 3 also shows the width and shape of the height distribution curve, which contains information about the smoothness of the deposited film. It was first suggested by Hansma et al.,⁸ that the PTFE-oriented structure may be derived, in part, from the multitude of ridges forming in the film. These ridges can presumably provide effective nucleation sites to induce the unidirectional growth of a variety of materials. The adjacent spacing measured between ridges ranging from about 0.01–0.2 μm , and ridges as high as 80 Å above the average film thickness were occasionally observed.

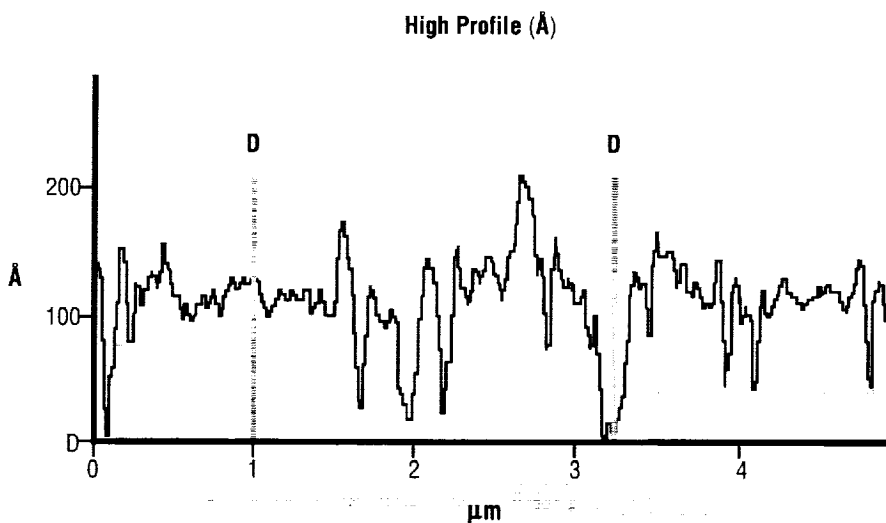


Figure 3. Film thickness distribution curve, measured at the cross-sectional line. The average film thickness was determined to be about 120 Å.

3.2 Atomic Resolution of PTFE Macromolecules

Figure 4 is an atomic resolution image, taken at a 50-Å field of view, shows that the chain-like structure of the PTFE macromolecules are aligned parallel to each other with an average intermolecular spacing of 5.72 Å. Previously, an AFM investigation from Dietz et al.¹⁰ found that the average intermolecular spacing for highly oriented PTFE molecule is ≈ 5.80 Å. However, a smaller value for the PTFE intermolecular spacing, ≈ 5.3 Å, was reported by Magonov et al.⁹ In addition, Bunn and Howells¹¹ found from their x-ray diffraction studies that these molecules are packed on a nearly hexagonal array with an intermolecular spacing of 5.54 Å, which is in good agreement with the results of this report. PTFE is known to have a very low coefficient of friction, and suggests that this remarkably low friction property could be derived from the inherently low cohesive forces between the adjacent molecular chains. In figure 4, the bright spots positioned periodically along the molecular chains indicate the high elevations from the top layers of the fluorine helix chain atoms.

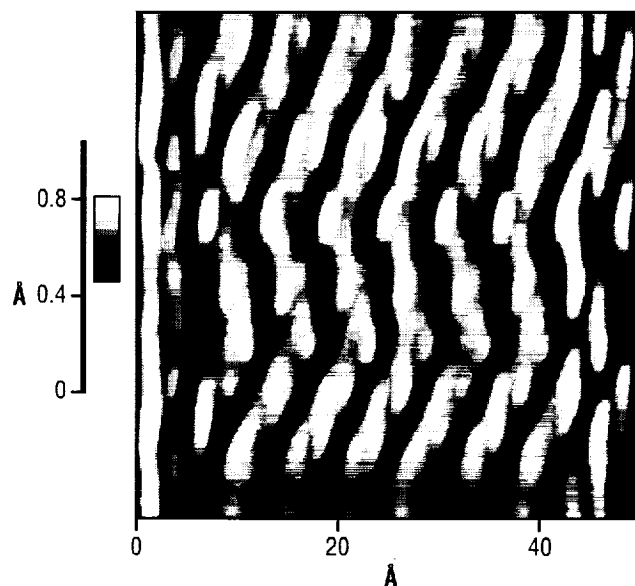


Figure 4. Atomic resolution image taken with a 50-Å field of view, shows the chain-like structure of the PTFE macromolecules with intermolecular spacing of 5.72 Å

Figure 5 shows the unique helical structure of the macromolecules, presumably produced by individual fluorine chain atoms. Both images were processed using flatten and noise reduction Fourier-filtering mode.

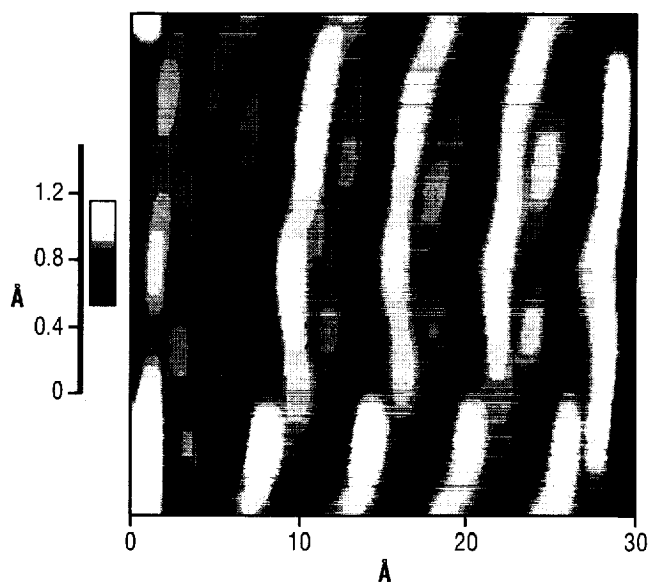


Figure 5. Image is taken with a 30-Å field of view, showing the unique twisted character of the macromolecules.

3.3 Atomic Resolution of Fluorine Atoms

Figure 6 is an unfiltered image, taken with a 25-Å field of view, showing four PTFE macromolecules that are aligned parallel to each other. Figure 3 is the same image, after applying the Fourier-filtering mode, that shows clearly, for the first time, each individual fluorine atom positioned along each of the four molecular chains. According to the PTFE molecular model given by Bunn and Howells,¹¹ one would expect to see a specific period length that is repeatable for every 13th chain atom positioned along each molecular chain. In this model, the molecular length for one period is about 16.8 Å, and half of this period length is 8.4 Å. This one-half period is observed from figure 7 as one “loop” distance measured between two adjacent “nodes” along the molecular chain. The average period length for a 13-chain atom was found to be 16.9 Å, which is in excellent agreement with the x-ray diffraction studies. Interestingly, the very first PTFE molecule, viewing from left to right in figure 7, has no strong observable evidence for a twist or node. In other words, this molecule appears as if it has been “untwisted” to clearly reveal two-line molecular chains. Evidently, figure 4 also reveals that there is variation for the chain periods as observed along each of the PTFE molecules. It is speculated that these thin films may have produced a different PTFE configuration that consists of many different chain length periods. Indeed, AFM observation of different chain periods has been reported previously by Magonov et al.⁹

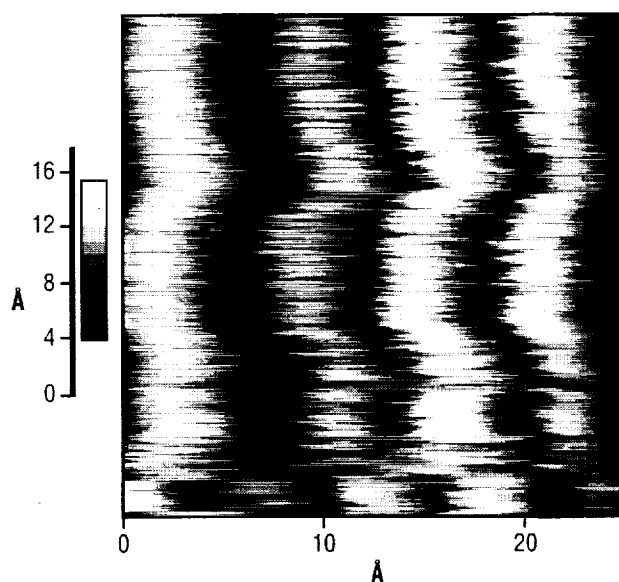


Figure 6. Unfiltered atomic resolution image, taken at a 25-Å field of view, shows four PTFE macromolecules that are aligned parallel to each other.

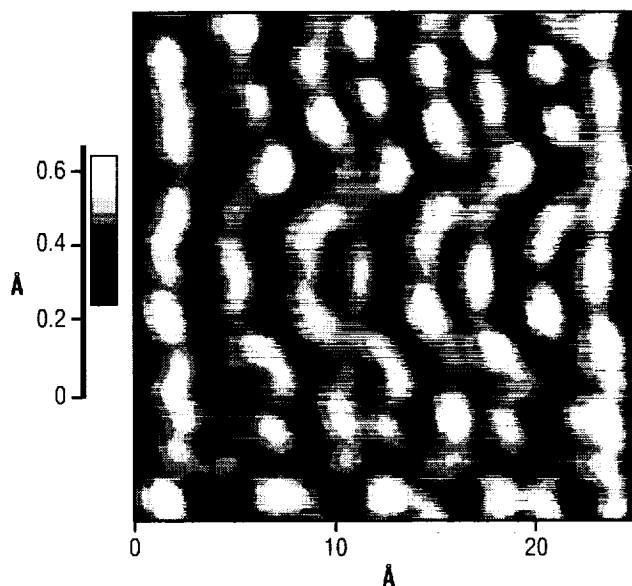


Figure 7. Image similar to figure 6, but after applying the Fourier-filtering mode, which clearly shows each individual fluorine atom positioned along each of the PTFE macromolecular chains.

Furthermore, the first direct AFM measurements for the radius of the fluorine-helix, and of the carbon-helix in sub-angstrom scale are reported as 1.70 and 0.54 Å, respectively. It is suggested that this report is the first direct observation of individual fluorine atoms and the measurement of the fluorine-helix and carbon-helix radii from highly oriented PTFE films using AFM. These measurements were based on the fact that the AFM microscope was calibrated in x and y scanning directions by imaging the well-known hexagonal structure of muscovite mica, which has a lattice spacing of 5.20 Å. In summary, table 1 shows the direct AFM measurements for the PTFE molecular configuration in comparison with other AFM studies^{9,10} and x-ray diffraction data.¹¹ Clearly, the AFM measurement results show only a small discrepancy in dimensional values as compared with data from the x-ray or electron diffraction.

Table 1. X-ray diffraction and AFM measurements comparison for PTFE molecules.

PTFE Molecular Configuration	X-Ray Diffraction	AFM Techniques		
	Ref. 11 (Å)	This Report (Å)	Ref. 10 (Å)	Ref. 9 (Å)
PTFE Intermolecular Spacing	5.54	5.72	5.80	5.30
Bragg Spacing Along Chain Axis	1.29	1.43	–	–
Fluorine Atomic Spacing	2.60	2.75	–	–
Period Length (13-Atom Chain)	16.8	16.9	11.4	–
CF ₂ Group Helix Spacing	2.0–2.4	2.36	–	–
Fluorine-Helix Radius	1.64	1.70	–	–
Carbon-Helix Radius	0.42	0.54	–	–

4. CONCLUSIONS

This technical memorandum reports the first direct observation of individual fluorine atoms, and the measurement of the fluorine-helix and carbon-helix radii from highly oriented PTFE films. Previously, there were some AFM investigations of the PTFE molecular structure performed by other researchers; however, image resolution from these studies was not sufficient to clearly distinguish the individual fluorine atoms from the PTFE macromolecular chains. The results demonstrate the unique capability of AFM for surface analysis of polymer thin films, in particular, for PTFE macromolecules on the atomic scale. Results from this study suggest that AFM image resolution of nonconductive materials may be higher than that achieved by transmission electron microscopy in some instances.

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